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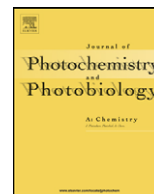
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Photocatalytic bleaching of p-nitrosodimethylaniline and a comparison to the performance of other AOP technologies

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ABSTRACT

In this paper, the performance of a developed photo reactor has been studied using the process of bleaching of p-nitrosodimethylaniline (RNO). The effect of available surface area in the reactor has been tested with the TiO₂ suspension system as reference, as well as the influence of operating parameters as pH and aerobic/anaerobic conditions. The bleaching of RNO by UV light alone was found to be significantly slower compared to the bleaching observed when applying photocatalysis, but the initial bleaching rate when applying TiO₂ in suspension was still 7 times faster compared to the most efficient immobilized TiO₂ treatment set up. An approximate linear correlation between the surface area of the TiO₂ available for reaction and the initial rate of bleaching was found. In addition, the kinetics of the photocatalytic bleaching was found to obey L–H kinetics. The pH of the solution was found to influence the rate of bleaching presumably due to the change in the surface charge of TiO₂. Also aerobic/anaerobic conditions and the presence of hydroxyl radical scavenger had a profound influence on the bleaching rate, where the reductive bleaching process was found to be much faster than the oxidative bleaching paths. When comparing the obtained rates of bleaching of RNO in the photocatalytic reactors to two competitive AOPs, UV/S₂O₈²⁻ and conductive-diamond electrochemical oxidation (CDEO), the CDEO process was the most energy efficient for bleaching of RNO.

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1. Introduction

Advances in chemical water and wastewater treatment have led to the development of methods termed advanced oxidation processes (AOPs), broadly defined as aqueous phase oxidation methods based on highly reactive radical species, primarily but not exclusively hydroxyl radicals, leading to the destruction of the pollutants [1]. Over the past 30 years, the efforts in research and development of AOPs have increased dramatically particularly for two reasons; the diversity of technologies involved and the areas of potential applications [1]. Key AOPs include heterogeneous and homogeneous photocatalysis based on near ultraviolet (UV) or solar visible irradiation, electrolysis, ozonation, Fenton's reagent, ultrasound (US) and wet air oxidation (WAO). Although water and wastewater treatment is by far the most common area of research, AOPs have also found applications in groundwater treatment, soil remediation, municipal wastewater sludge conditioning, ultrapure water production, volatile organic compound treatment and odour control.

In heterogeneous photocatalysis a semiconductor, usually TiO₂, is activated by UV irradiation. In this process, completely mineralization of organic pollutants to carbon dioxide and inorganic acids can be achieved. The initial step of photocatalysis is the generation of electron–hole pairs within the TiO₂ particle:



The photogenerated holes have been suggested directly to oxidize adsorbed molecules or to react with surface hydroxyl groups or water molecules to produce hydroxyl radicals [2–4]:



The photogenerated electrons (e[−]) have been suggested to be trapped by oxygen or surface defect sites, which in turn diminish the recombination of the photogenerated electron–hole pairs and hence enhance the photocatalytic activity [2,4,5]. The reduction potential for the conduction band electrons is −0.52 V, however, the electrons may become trapped and loose some of their reducing power [2]. The species generated from the electron–hole pair include hydroxyl radicals (HO•), superoxide (O₂[−]), and hydrogen peroxide (H₂O₂).

In several studies, aqueous suspensions of TiO₂ particles have been investigated in different kinds of photo reactors for potential

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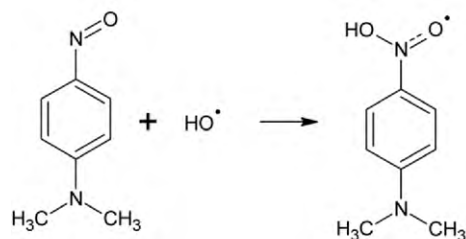


Fig. 1. The oxidation of p-nitrosodimethylaniline by the hydroxyl radical. The second order rate constant is determined to $1.25 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [2].

use in water treatment. The use of TiO_2 in suspension is efficient due to large surface area of the catalyst available for reaction and due to the absence of mass transfer limitations. However, the use of suspensions requires an additional separation step, which is both time consuming and expensive [3,6,7]. In order to overcome some of these obstacles, much attention has been directed towards photo reactors in which the TiO_2 catalyst is immobilized. There have been made numerous attempts to immobilize TiO_2 on different substrates in order to maximize the surface area of the catalyst as the reaction occurs at the liquid–solid interface [8–11]. However, many of the proposed photo reactors in literature suffer from non-uniform irradiation in which only some of the TiO_2 is activated [9,12].

In this paper, the bleaching of the organic dye p-nitrosodimethylaniline (RNO) by heterogenous photocatalysis has been studied. RNO is chosen as test subject, since it is a very applicable and easy to use compound for evaluation of the oxidation power in the design and optimization of reactors for AOP, taking account of several oxidative species generated in the process [13]. In aqueous solution it gives a strong yellow colour owing to the system of well structured conjugated double bonds in the molecule (Fig. 1), and the oxidative performance of the AOPs is followed by absorbance measurements at the strong absorption band at 440 nm by UV/vis spectroscopy. RNO is primarily applied as a spin trap for the detection of hydroxyl radicals (Fig. 1), as it neither reacts with singlet oxygen ($^1\text{O}_2$), superoxide anions (O_2^-) or other peroxy compounds [14–17]. However, ozone, hypochlorous acid and hypochlorite are other strong chemical oxidants, which besides the hydroxyl radicals have been shown to bleach RNO by chemical oxidation [13,18]. The rate of RNO bleaching was used to evaluate the performance of a developed photo reactor with respect to the TiO_2 surface area available of reaction, pH and aerobic/anaerobic conditions. Finally, the efficiency of the photocatalytic bleaching of RNO is compared to the bleaching obtained by two other AOPs: the

Table 1

Details on the photo reactor and experimental settings.

Reactor type	Stainless steel tubular with centred UV lamp ($l = 31 \text{ cm}$, $d = 6 \text{ cm}$)
TiO_2 coated liner	The liner consists of 26 stainless steel discs ($d = 5.5 \text{ cm}$) installed perpendicular to the UV lamp
UV lamp	14 W low pressure lamp (254 nm, 20 mW cm^{-2})
Flow rate	300 L h^{-1}
Initial RNO conc.	$2.5\text{--}10 \text{ mg L}^{-1}$ ($(1.66\text{--}6.66) \times 10^{-5} \text{ M}$)
Total volume	3 L
pH range	4–10
Temperature	$20 \pm 1^\circ \text{C}$

UV/ $\text{S}_2\text{O}_8^{2-}$ process and the conductive-diamond electrochemical oxidation (CDEO) process.

2. Materials and methods

The investigation of the bleaching of RNO in the different reactors (UV reactor/photocatalytic reactor with immobilized $\text{TiO}_2/\text{TiO}_2$ suspension reactor) has been performed in a batch system, where the RNO solution was recycled from a water cooled reservoir through the reactor (Fig. 2). The performance of the following reactor setups was investigated: UV light, UV light + TiO_2 coated reactor wall, UV light + TiO_2 coated liner, and TiO_2 in suspension. The details of the photo reactor used and the experimental settings are summarized in Table 1. The internal wall of the photo reactor and the liner were in steps coated with a TiO_2 suspension produced by an in-house developed microwave assisted sol–gel method resulting in particles mainly consisting of anatase and a lower amount of amorphous material. The TiO_2 production and dip coating procedure is in relation to procedures previously reported elsewhere [19]. When coated onto the stainless steel reactor wall and liner it forms a homogenous TiO_2 coating with an estimated thickness of 500 nm, based on profilometry studies. In the case of the TiO_2 suspension $50 \text{ mg Degussa P25 L}^{-1}$ solution (surface area $50 \text{ m}^2 \text{ g}^{-1}$) was used.

The bleaching of RNO was followed by UV/vis absorbance measurements at the significant absorption band of 440 nm by a Varian Cary 50 spectrophotometer. In experiments using TiO_2 suspensions, the samples obtained at given time intervals were subject to centrifugation and filtration (pore size $0.2 \mu\text{m}$) in order to remove the TiO_2 catalyst from the system.

The absorbance of RNO at 440 nm decreases dramatically under acidic conditions, but remains constant in the neutral and alkaline pH range. Therefore, samples obtained from experiments conducted under acidic conditions were pH adjusted before

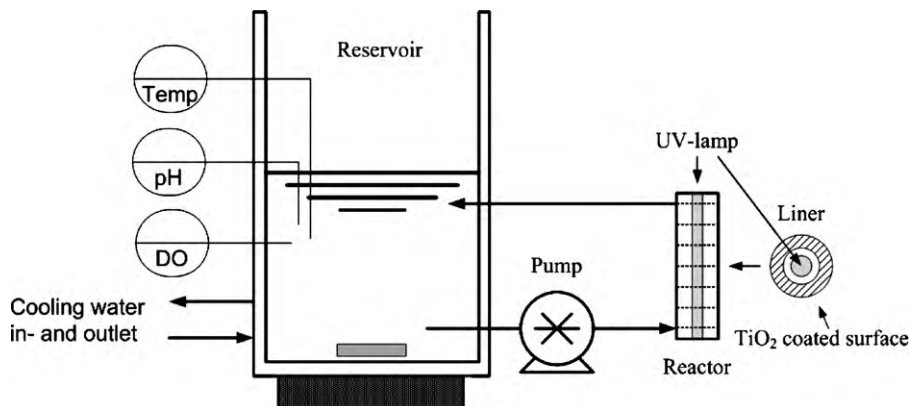


Fig. 2. The experimental set up based on batch recirculation from a water cooled reservoir through the photo reactor.

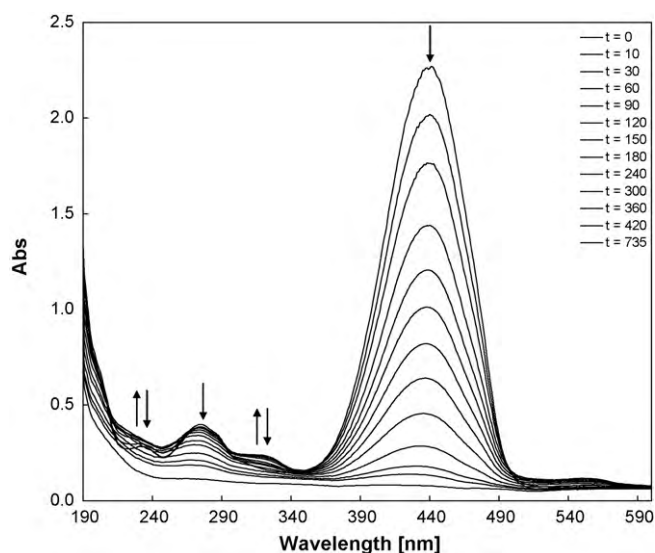


Fig. 3. Bleaching of RNO in photo reactor with TiO₂ coated liner in air saturated solution at pH 6.2.

measurement. The temperature, oxygen saturation and pH were monitored with sensors in the reservoir. Experiments were conducted under both aerobic and anaerobic conditions and with and without the addition of a hole/hydroxyl radical scavenger in the form of tert. butanol (conc. 0.10 M). If not stated otherwise the experiments were conducted at air saturation where air was bubbled through the solution during the experiment. Anaerobic conditions were obtained by bubbling N₂ gas through the solution in order to remove O₂ from the system.

3. Results and discussion

3.1. Bleaching of RNO

The bleaching/degradation of RNO can be investigated from the changes in the UV/vis absorption spectra recorded after different UV irradiation times. Fig. 3 shows the bleaching of RNO in the photo reactor with TiO₂ coated liner. The absorption peaks corresponding to the dye decreases and finally disappears after continued recirculation through the photo reactor for a period of 735 min. The proposed mechanism for the bleaching is suggested to proceed through an oxidation process in which trapped holes or hydroxyl radicals react with the conjugated double bonds in the π system of RNO. This process is thermodynamic favoured as the valence band of TiO₂ (+2.5 V versus NHE at pH 7) is much higher than the oxidation potential of RNO (+0.3 V versus NHE at pH 7) [20]. The appearance and later disappearance of absorption bands located at 240 and 320 nm is assigned to formation and degradation of aromatic intermediates.

The bleaching of RNO in the photo reactor operated under different conditions is shown in Fig. 4: UV light, UV light + TiO₂ coated reactor wall, UV light + TiO₂ coated liner, and TiO₂ suspension. The bleaching of RNO by UV light alone was found to be significantly slower compared to the bleaching in the photocatalytic reactors. Comparison of the initial rates of bleaching showed an increase in the rate of bleaching of a factor of 4 (TiO₂ coated reactor wall) and 8.5 (TiO₂ coated liner) for the immobilized photocatalytic reactors compared to UV bleaching alone. The highest bleaching rate was found in the TiO₂ suspension photocatalytic reactor. In the latter case the initial rate was found to increase by a factor of 62.5 compared to the pure photo bleaching process. The significantly higher rate of bleaching found in the case of the TiO₂ suspension reactor is

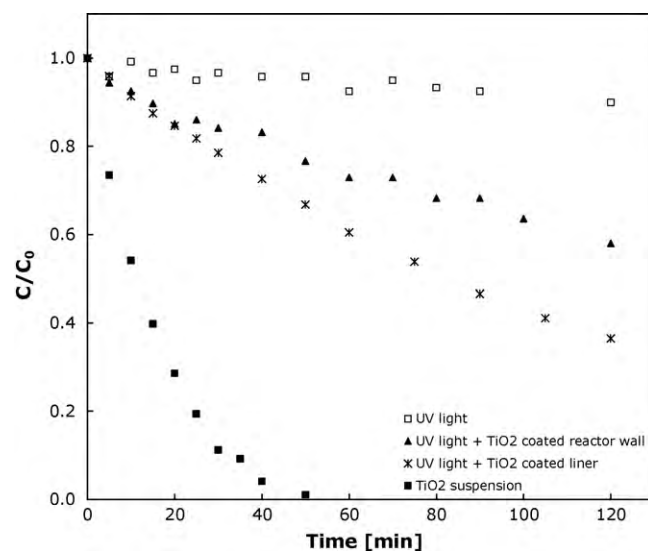


Fig. 4. Comparison on the photocatalytic bleaching of RNO in different photo reactor in air saturated solution at pH 6.2.

due to the larger surface area of the catalyst available for reaction and due to the absence of mass transfer limitations. However, the use of suspensions requires an additional separation step which is both time consuming and expensive. Thus the immobilized photocatalytic reactors are more applicable in practice. In this work the TiO₂ suspension reactor was used as a reference for the maximum achievable rate of bleaching of RNO using photocatalysis in the applied set up. Comparison of the different photo reactors used in this investigation showed that an approximate linear correlation between the surface area of the TiO₂ available for reaction and the initial rate of bleaching was found. Even though the TiO₂ coated liner increased the area considerable compared to the photo reactor with the TiO₂ coated reactor wall, still much higher surface area was available for reaction in the case of suspended TiO₂ particles.

3.2. Kinetic investigation

The bleaching of RNO in the photo reactor with TiO₂ coated liner was examined at different initial concentrations (Fig. 5). In the absence of TiO₂, bleaching of RNO was found to follow slowly zero

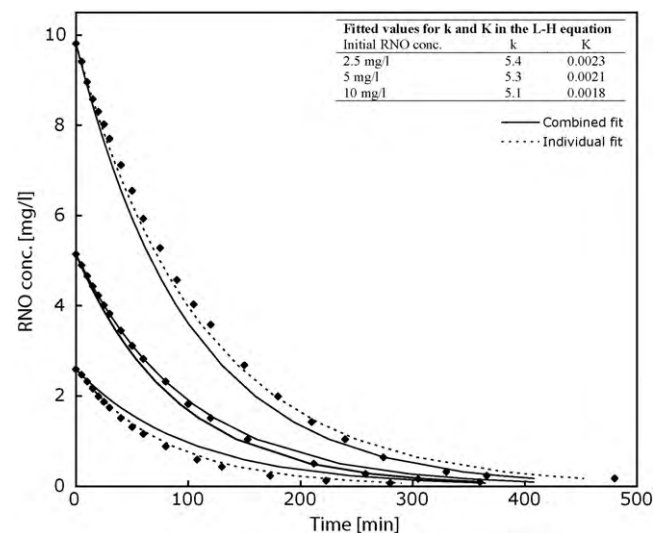


Fig. 5. L-H fit to the photocatalytic bleaching of RNO in the photo reactor with TiO₂ coated liner in air saturated solution at pH 6.2.

order kinetics. In the presence of the TiO₂ coated liner the bleaching of RNO will occur: (i) as a pseudo first order reaction taking place on the TiO₂ surface (rate r_1) and (ii) as a zero order reaction (rate r_2) similar to that of the TiO₂ free system. Thus, the observed degradation rate (r_{obs}) in the photo reactor should be the sum of the two reactions rates:

$$r_{\text{obs}} = r_1 + r_2 \quad (4)$$

The initial rate found for the 10 mg L⁻¹ initial concentration system, $r_{\text{obs}} = 0.08 \text{ mg L}^{-1} \text{ min}^{-1}$ ($8.9 \times 10^{-9} \text{ M s}^{-1}$) is one order of magnitude greater than $r_2 = 0.007 \text{ mg L}^{-1} \text{ min}^{-1}$ ($7.8 \times 10^{-10} \text{ M s}^{-1}$), thus the photo bleaching has minor effect on the photocatalytic bleaching.

The photocatalytic degradation of many organic compounds has often been modelled to Langmuir–Hinshelwood (L–H) kinetics [3,4]:

$$r = \frac{dC}{dt} = \frac{kKC}{1 + KC} \quad (5)$$

where k is the rate constant and K is the adsorption constant. From Fig. 5 it is seen that L–H kinetics fits the experimental data obtained at different initial RNO concentration (individual fit). By averaging the parameters k and K for the different initial concentration experiments also a good combined fit was obtained with the values $k_{\text{av.}} = 5.2 \text{ mg L}^{-1} \text{ min}^{-1}$ ($5.8 \times 10^{-7} \text{ M s}^{-1}$) and $K_{\text{av.}} = 0.0019 \text{ L mg}^{-1}$ ($2.9 \times 10^2 \text{ L mol}^{-1}$) suggesting that the bleaching of RNO can be described by L–H kinetics.

To investigate the nature of the reaction kinetics in greater detail, a reducing agent (tert. butanol) was used as hole/hydroxyl radical scavenger to compete with RNO oxidation. The addition of tert. butanol resulted in a slight decrease in the rate of bleaching. In addition, experiments were conducted under anaerobic conditions. Oxygen is usually suggested to function as electron trap preventing recombination of the electron–hole pair. Thus under anaerobic conditions the rate of degradation will typically be lower. The reduction potential of RNO has been reported to be +0.04 V versus NHE at pH 7.0 determined by cyclic voltammetry [20], which is higher than the conduction band of TiO₂ (−0.52 V) suggesting that the photo generated conduction band electrons are able to reduce RNO. Experiments conducted under anaerobic conditions (Fig. 6) showed that the rate of bleaching of RNO increased slightly under anaerobic conditions. In this case the bleaching of RNO may be due to both

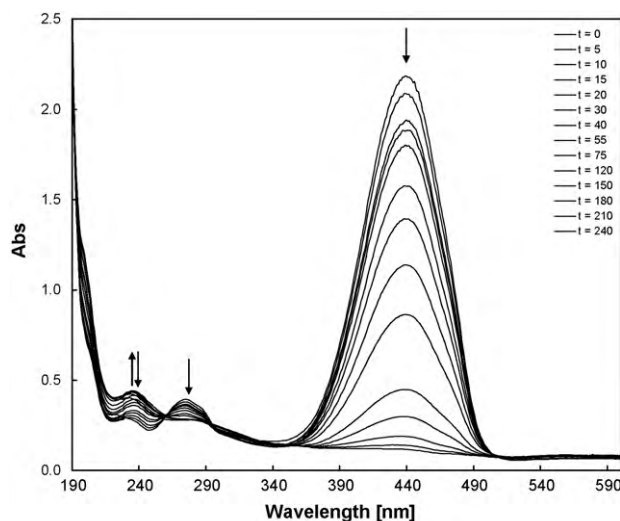


Fig. 7. Bleaching of RNO in photo reactor with TiO₂ coated liner under anaerobic conditions and hole/hydroxyl radical scavenger at pH 6.2.

an oxidative and reductive mechanism. Furthermore, experiments were conducted with the addition of tert. butanol as hole/hydroxyl radical scavenger under anaerobic conditions (Fig. 6). These experiments clearly show that RNO can be bleached by a reductive mechanism as the rate of bleaching considerably increases under anaerobic conditions and even more when a hydroxyl scavenger is added. In aerobic conditions, where molecular oxygen functions as electron scavenger, the bleaching of RNO is slower compared to bleaching observed under anaerobic conditions. This means that bleaching performed by the reduction processes are faster than the oxidative bleaching processes. The role of oxygen as electron scavenger results in an overall slower process. On the contrary, if a hole/hydroxyl radical scavenger is added under the anaerobic conditions, the hole/electron recombination process is reduced, resulting in an increased rate of bleaching. The reduction process is believed to bring an electron into the antibonding π -electron system of RNO giving rise to a decrease of the total bonding energy of the π -electron system, which may also results in bond cleavage.

In addition, further experiments showed that the reduced form of RNO could not be re-oxidized by purging the solution with air, which supports the provided explanation above.

Comparison of the UV/vis absorption spectra of the bleaching of RNO under anaerobic/scavenger (Fig. 7) and aerobic conditions (Fig. 3) shows that a new absorption band appears in the spectrum around 230 nm. This absorption peak may be assigned to reduced bleaching intermediates.

3.3. Effect of pH

The adsorption on TiO₂ depends to a great extent on the surface charge, which in turn varies as a function of pH of the solution. The point of zero charge (pzc) for TiO₂ has been reported to several values within the pH range of 6.0–6.8 [7]. The TiO₂ surface is positively charged in acidic media (pH < 6) whereas it is negatively charged under neutral and alkaline conditions (pH > 6).

The UV/vis spectrum of RNO in aerobic aqueous solution remains unchanged in the pH range of 6.2–10, but changes below pH 6.2 due to protonation, where the maximum absorption peak shifts to 350 nm [14]:



The loss of absorbance is proposed to be caused by proton interactions with one of the lone pairs of the nitrogen atoms in

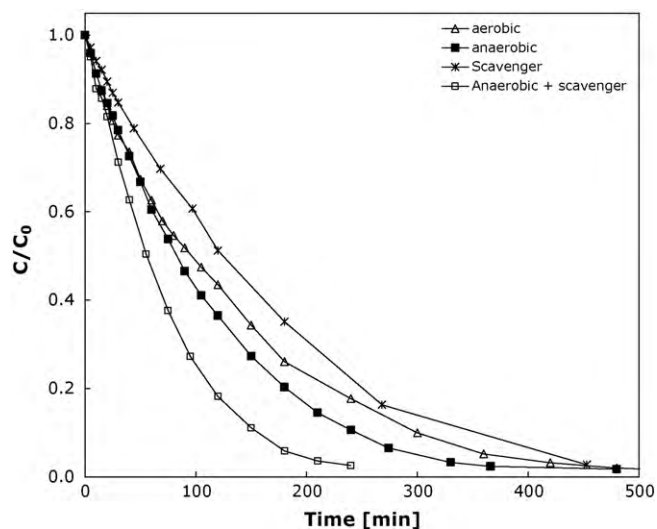


Fig. 6. Bleaching of RNO under aerobic and anaerobic conditions with and without tert. butanol as hole/hydroxyl radical scavenger in the photo reactor with TiO₂ coated liner in air saturated solution at pH 6.2.

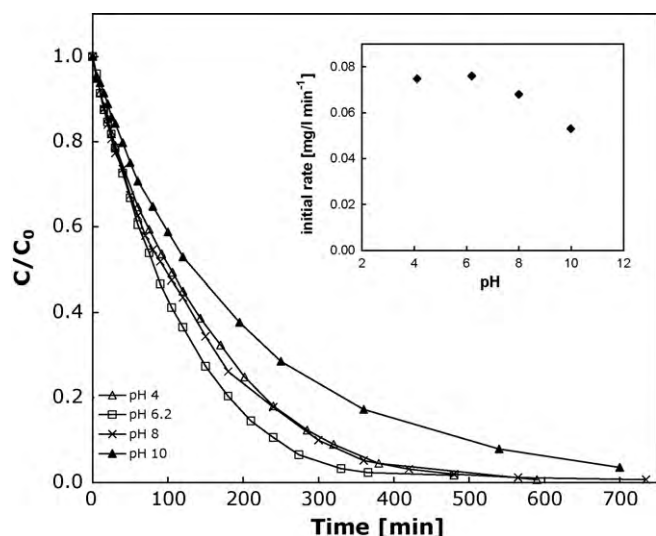


Fig. 8. Bleaching of RNO in the photocatalytic reactor with TiO_2 coated liner in air saturated solution at different pH. Inserted graph: initial rate of bleaching of RNO as a function of pH.

RNO, either in the tertiary amine group or more probably in the nitroso group, which in the acidic environment disrupt and fixate the conjugated double bond system changing the light absorption properties.

Since the structure of RNO is intact in the pH range 6.2–10, any changes in the initial degradation rate with varying pH values can be ascribed to variations of the acid/base properties of the TiO_2 surface. In Fig. 8, the bleaching of RNO in the pH interval from 4 to 10 is shown. From the subplot in Fig. 8 it is seen that the highest bleaching rate is found at pH 6.2, where both the RNO molecule and the TiO_2 surface have low surface charge. At low pH, the protonated RNO is repelled by the positively charged TiO_2 surface, whereas the increasingly negatively charged TiO_2 at increasing pH values above the pzc retard the absorption of the neutral RNO molecule resulting in slower initial degradation rates (Fig. 8). However, these results contradict the trends of pH influence of photocatalytic RNO bleaching reported by Zang et al. (1997) [20].

Comparison of the UV/vis absorption spectra for the photocatalytic bleaching of RNO obtained at pH 6.2 and 10 suggests that the bleaching/degradation mechanism may be different at pH 6.2 and 10. In the case of pH 6.2, an increase in the absorption bands located at 240 and 320 nm was observed, whereas at pH 10 an increase in the narrower absorption bands located at 260 and 320 nm was observed. The differences in the UV/vis spectra may arise from oxidation of pre-adsorbed RNO molecules in case of pH 6.2 due to a higher adsorption of RNO to the TiO_2 surface at this pH compared to the adsorption at pH 10, where the bleaching may be more attributed to oxidation by hydroxyl radicals in the near surface region.

3.4. Comparison to $\text{UV/S}_2\text{O}_8^{2-}$ and CDEO

RNO has showed to be a very applicable compound for optimization of different kinds of advanced oxidation techniques with regards to reactor design, operating parameters, etc. [13], in order to obtain fast reaction rates in combination with high efficiencies. In this sense, the bleaching performance obtained by the photocatalytic reactor system has been compared to similar bleaching studies of RNO by two other advanced oxidation techniques; the $\text{UV/S}_2\text{O}_8^{2-}$ process generating both sulphate and minor amounts of hydroxyl radicals through the photolysis of added peroxodisulphate, and the fundamentally different conductive-diamond

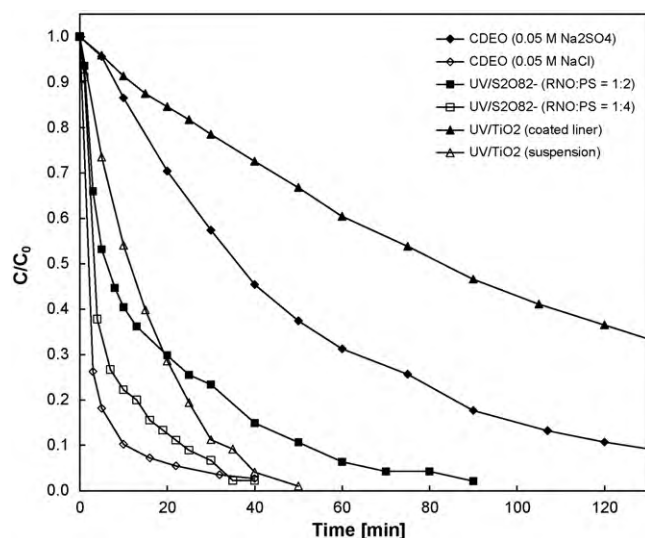


Fig. 9. Time course of solution absorbance measured at 440 nm for the three advanced oxidation processes (AOPs). Each AOP is represented by two sets of operating parameters.

electrochemical oxidation (CDEO) process applying silicon-based boron-doped diamond electrodes (Si-BDD), where hydroxyl radicals are produced at the surface of the anode due to water discharge [21]. The full studies applying these AOPs for bleaching of RNO are currently in the pipeline for scientific publication. All of the three AOPs require use of additional chemical substances besides the applied energy sources (UV lamps and electrochemical cell) in order for the processes to operate; titanium dioxide as photocatalyst in the UV/TiO_2 process (suspension or immobilized), peroxodisulphate as oxidant in the $\text{UV/S}_2\text{O}_8^{2-}$, and sodium sulphate and sodium chloride as electrolytes in the electrochemical oxidation process. The comparison between the three AOP techniques was based on a combination of rate of bleaching and amount of energy used. Two experiments by each AOP conducted at different operating parameters were considered. In Fig. 9, the relative changes in absorbance with time from the six experiments are showed. It is difficult to compare the RNO bleaching efficiency of the AOPs directly from Fig. 9 due to the different conditions under which the experiments were conducted.

A pseudo first order model could in all of the experiments with some approximation be used as model for the bleaching rates observed. When calculating the half lives of the bleaching reactions (Table 2) it is seen that the electrochemical oxidation in a chloride electrolyte was the fastest process. In this case, RNO is bleached both indirectly in the bulk solution by active chlorine species produced by chloride electrolysis and directly at or near the anode surface by electrochemically generated hydroxyl radicals. The processes of UV/TiO_2 coated liner and CDEO in 0.05 M Na_2SO_4 are both processes, which are dependent on that the hydrodynamic conditions in the reactor/cell provide high mass transfer of the RNO in bulk solution to the oxidative processes on the surface. As it is showed in Fig. 9 and Table 2, the electrochemical oxidation process was the fastest in this comparison. The rates of bleaching are highly dependent on the operating parameters used when applying the AOPs (concentration of peroxodisulphate and sodium chloride, current intensity, treated volume, etc.). Thus a better measure of AOP efficiency is the energy consumption per litre of treated water. By this mean of comparison the chloride mediated CDEO process was still the most efficient with the lowest energy consumption in order to remove 90% of the solution absorbance. However, the photocatalytic process with TiO_2 in suspension was much more energy efficient compared to the $\text{UV/S}_2\text{O}_8^{2-}$ process, where a high

Table 2

Figures of merit for the AOPs regarding reaction rates of first order bleaching and energy consumption.

	Energy source	k/s^{-1}	$t_{1/2}/\text{min}$	Energy consumption (90% bleaching)/ kWh m^{-3}
CDEO (0.05 M Na_2SO_4)	Power supply (10.6 W)	3.1×10^{-4}	36.9	7.2
CDEO (0.05 M NaCl)	Power supply (12.0 W)	3.6×10^{-3}	3.2	0.7
UV/ $\text{S}_2\text{O}_8^{2-}$ (RNO: $\text{S}_2\text{O}_8^{2-}$ = 1:2)	UV lamp (400 W)	6.5×10^{-4}	17.9	19.8
UV/ $\text{S}_2\text{O}_8^{2-}$ (RNO: $\text{S}_2\text{O}_8^{2-}$ = 1:4)	UV lamp (400 W)	1.5×10^{-3}	7.8	8.6
UV/ TiO_2 (coated liner)	UV lamp (14 W)	1.6×10^{-4}	73.0	18.9
UV/ TiO_2 (suspension)	UV lamp (14 W)	1.4×10^{-3}	8.0	2.1

power 400 W lamp was used in order to generate the sulphate radicals. Generally considered, the electrochemical oxidation process applying the Si-BDD anodes proved in this comparison to be the most efficient advanced oxidation process for the bleaching of RNO.

4. Conclusions

The rate of bleaching of the organic dye p-nitrosodimethylaniline (RNO) has been used to evaluate the performance of a TiO_2 coated photo reactor for use in photocatalytic water treatment. The bleaching of RNO by UV light alone was found to be significantly slower compared to the bleaching observed when applying photocatalysis, but the initial bleaching rate when applying TiO_2 in suspension was still 7 times faster compared to the most efficient immobilized TiO_2 treatment set up. A good correlation between the surface area of the TiO_2 available for reaction and the initial rate of bleaching was found. In addition, the kinetics of the photocatalytic bleaching was found to obey L–H kinetics. The pH of the solution was found to influence the rate of bleaching presumably due to the change in the surface charge of TiO_2 . Also aerobic/anaerobic conditions and the presence of hydroxyl radical scavenger had a profound influence on the bleaching rate. When comparing the obtained rates of bleaching of RNO in the photocatalytic reactors to two competitive AOPs, UV/ $\text{S}_2\text{O}_8^{2-}$ and conductive-diamond electrochemical oxidation (CDEO), the CDEO process was the most energy efficient for bleaching of RNO.

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